On the question of electrolytic metal overvoltage

By
T. Erdey-Grúz and M. Volmer

(With 13 figures in text.)

(Received on 04.09.31)

Zeitschrift für Physikalische Chemie, Band 157, Nr. 3/4, 1931, Seite 165–181.

Abstract

The various characteristics that theoretically result from the various possibilities of the partial process that determines the rate of electrolytic metal deposition are discussed. Using the experimental current-voltage curves and the microcinematographic recordings, the role of the active sites is pointed out and a qualitative interpretation of the metal deposition is given.

1 Introduction

The electrolytic deposition of metals, one of the most important and seemingly simplest electrochemical processes, is a problem that is still far from being fully understood. The hydrated metal ion in the solution only finds its final place in the crystal lattice of the cathode through various intermediate states. If all phases of the process were to proceed uninhibited, then one would expect that metal electrolysis would occur at low current densities without noticeable polarization. Polarization would only be expected at current densities at which the depletion of the solution layer on the cathode becomes noticeable. This concentration polarization depends, *ceteris paribus*, only on the diffusion coefficient of the electrolyte. The diffusion coefficient is only slightly different for the different electrolyte solutions. If only concentration polarization were the main point in metal electrolysis, the same current densities would have to cause approximately the same polarization voltages for all metals. But as we know, this is far from being the case. While with mercury electrodes the polarization voltage only reaches the order of magnitude of 1 mV at current densities of 5 mA to 10 mA, similar polarization voltages may be found in solid metals at current densities that are 100 to 1000 times smaller (so-called chemical polarization, [6]). Since, according to what has been said above, the concentration polarization and any co-measured Ohmic voltage drop (see below) should in all cases be of the order

of magnitude of the amount that it would be under similar conditions with a mercury electrode, there must be other causes here.
To investigate the causes of chemical polarization (we will call it metal overvoltage), examining the current-voltage curves is the appropriate way. The metal overvoltage is but caused by the slowness of one of the deposition processes. The shape of the current-voltage curves is therefore determined by the type and potential dependence of the rate-determining process. From the shape of the current-voltage curves one can therefore extrapolate to the rate-determining process.

2 Causes of Overvoltage and the Characteristics of the Partial Process

When asked about the slowest part of the metal deposition process that determines the overvoltage, the possibility of the slow supply of free ions from complexes or hydrates was pointed out a long time ago. Le Blanc and Schick, [7] have directly shown that the dissociation of complex ions can occur at a measurable speed. While the delayed supply of ions from complexes certainly plays a role in individual cases, in general it cannot explain the metal overvoltage any more than the slow dehydration of the ions assumed by Le Blanc, [6].
So, if we ignore the delays in the ion supply caused by the solution, the following possibilities come into question for the course of the metal deposition.

1. The *discharge* of the metal ions is the slowest process; the incorporation of the discharged ions into the crystal lattice of the cathode occurs quickly.
2. The incorporation into the crystal lattice, i.e. *the electrolytic crystal growth*, is the rate-determining process; the discharge itself occurs quickly without any noticeable inhibition at the points where the discharged ions are embedded in the lattice.

Let's see what kind of current-voltage curves these possibilities result in.

1. If the discharge of the cations determines the rate of electrolysis, the following relationship applies, as we were recently able to show, [3]:

$$\eta = a - b \cdot \log(J)\,, \tag{1}$$

   where η is the overvoltage, J is the current density, and a and b are constants. This case is known to occur in electrolytic hydrogen deposition.
2. If electrolytic crystal growth is the rate-determining process, the shape of the current-voltage curves depends on the way in which the formation and growth of the crystals takes place. In this case, the metal

deposition can take place in such a way that new lattice planes are formed mainly on the existing crystals and the formation of new crystal nuclei plays a subordinate role. However, it is also conceivable that the individual crystals can only grow unhindered to a very limited extent per lattice plane, so that the speed of metal deposition and thus also the overvoltage is primarily determined by the frequency of three-dimensional nucleation.

The two options require different current-voltage curves.

(a) If the *growth* of the crystals plays the decisive role, there are again two options:

(α) The growth rate is determined by the frequency of two-dimensional nucleation on the crystal surfaces; the supply of material to the growing points occurs so quickly that the growth of the growth-capable nuclei into complete lattice planes occurs without inhibition, i.e. quickly. If W_2 means the work required to form a nucleus capable of two-dimensional growth, then in this case the frequency of nucleation and thus the current density proportional to it can be calculated as a first approximation according to:

$$J = k_1 \cdot e^{-\frac{W_2}{kT}} . \tag{2}$$

Now, according to Brandes, [1], the two-dimensional nucleation work is:

$$W_2 = \frac{\pi \varrho^2 O}{kT \cdot \ln\left(\frac{p}{p_\infty}\right)} , \tag{3}$$

where ϱ is the specific free edge energy of the two-dimensional nucleus, O is the molar area requirement, p_∞ is the vapor pressure of the crystal, and p the vapor pressure of the nucleus. In our case, the necessary supersaturation $\frac{p}{p_\infty}$ for the nucleus capable of growth would determine the overvoltage:

$$\eta = \frac{\mathscr{R}\,T}{n\,\mathscr{F}} \cdot \ln\left(\frac{p}{p_\infty}\right) , \tag{4}$$

where n is the valence of the cation. It is therefore

$$W_2 = \frac{\pi \varrho^2 O}{n\,\mathscr{F}\,\eta} \tag{5}$$

and

$$J = k_1 \cdot e^{-\frac{\pi \varrho^2 O}{kTn\,\mathscr{F}\,\eta}} = k_2 \cdot e^{-\frac{k_2}{n\eta}} \tag{6}$$

(at constant temperature), if we ignore the change of the edge energy with the potential, which is allowed as a first approximation, and combine the constant quantities into k_2. It thus follows:

$$\ln(J) = \ln(k_1) - \frac{k_2}{n} \cdot \frac{1}{\eta} . \tag{7}$$

In this case the characteristic is a straight line when one plots $\log(J)$ against $\frac{1}{\eta}$.

(β) The second possibility is that the supply of material to the growing edges is slow, so that the growth of lattice planes and thicker layers has a significant influence on the deposition rate. In this case, as BRANDES pointed out, [2], a linear dependence of the overvoltage on the current density is to be expected. At the edges of the individual growing lattice planes and layers, metal deposition occurs without inhibition, so the overvoltage here is zero. An ion supply then takes place from the environment at the polarization potential, the current strength of which is proportional to this polarization potential (OHM's law). Since deposition occurs quickly at the edges, the supply of ions in the double layer is primarily the rate-determining factor, and the current strength of the metal deposition is proportional to the overvoltage.

(b) If the metal deposition is primarily determined by the frequency of three-dimensional nucleation, then the three-dimensional nucleation work W_3 is decisive. According to VOLMER and WEBER, [10], for spherical liquid nuclei the following relation holds:

$$W_3 = \frac{16\pi}{3} \cdot \frac{\sigma^3 \mathscr{M}^2}{d^2 \cdot \left[\mathscr{R} T \cdot \ln\left(\frac{p}{p_\infty}\right)\right]^2}, \tag{8}$$

where σ is the specific free surface energy, $\mathscr{M}$ the molar weight, and d is the density. If we apply this equation, which is valid for liquids, to crystals as a first approximation, then, taking Equation 4 into account, we get:

$$W_3 = \frac{16\pi}{3} \cdot \frac{\sigma^3 \mathscr{M}^2}{d^2 n^2 \mathscr{F}^2 \eta^2} = \frac{k_3}{n^2 \eta^2}, \tag{9}$$

if we neglect the potential dependence of σ (like that of ϱ above) and combine the constant quantities in k_4. It follows:

$$J = k_4 \cdot e^{-\frac{k_5}{n^2 \eta^2}} \tag{10}$$

and

$$\ln(J) = \ln(k_4) - \frac{k_5}{n^2} \cdot \frac{1}{\eta^2} \tag{11}$$

as a characteristic of this process.

In order to check which of the discussed assumptions applies in reality, one must use the experimental current-voltage curves to examine whether $\log(J)$ with η, with $\frac{1}{\eta}$, with $\frac{1}{\eta^2}$, or J with η shows a linear dependency. The area of small overvoltage is particularly of interest, since in this area of small supersaturation it is to be expected that one of the theoretically required curve shapes appears without disturbance. From this point of view, we examined the current-voltage curves of some metals.

3 Experimental Setup

The electrolysis was carried out in vessels that could be sealed airtight with paraffinized cork stoppers. The metal to be examined served as the cathode, and a much larger, cylindrically bent piece of the same metal served as the anode. The potential of the electrode examined was determined against a stationary electrode made of the same metal. This reference electrode was located in a LUGGIN capillary, the tip of which was pressed against the electrode being examined. The current strength was determined using a calibrated galvanometer. The potential difference occurring between the reference electrode and the examined electrode during electrolysis was determined using the POGGENDORFF compensation arrangement. In order to avoid undesirable polarization of the electrode being examined, a WULFF single-thread electrometer was used as the zero-instrument. With sufficient temperature protection of the latter, which was achieved by appropriate installation in a box filled with cotton, the potential measurement could be carried out with an accuracy of 0.2 mV. Some series of tests were recorded with a tube voltmeter described elsewhere with a sensitivity of 0.1 mV = 1 mm light pointer deflection.

All investigations were carried out with the exclusion of air in a nitrogen or hydrogen atmosphere. The gases (electrolytic bomb hydrogen, bomb nitrogen) were freed from oxygen and other impurities in the usual way. The solutions were usually saturated with hydrogen or nitrogen overnight, but at least for 2 hours, before the experiments.

In most cases analytically pure preparations from Kahlbaum were used. Otherwise the purest available variety was recrystallized several times. The electrodes were cemented with picein[1] into glass tubes.

We examined the current-voltage curves of Zn, Cd, Ni, Pb, Bi, Cu and Ag.

[1] An unreactive thermoplastic material consisting of a mixture of hydrocarbons with very low vapor pressure that adheres well to glass and metal. It is suitable as a sealant when assembling vacuum systems.

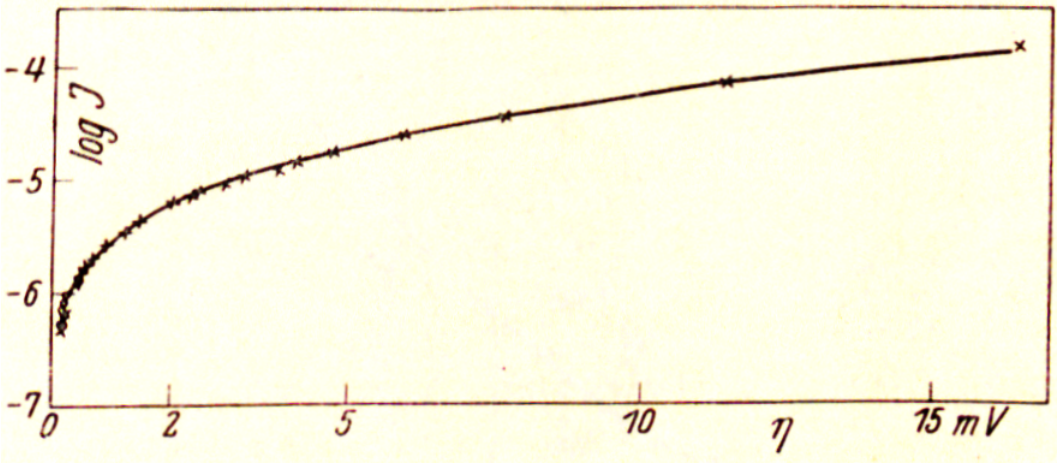


Figure 1: Zn in normal $ZnSO_4$-solution, saturated with H_2 $(\log(J) - \eta)$

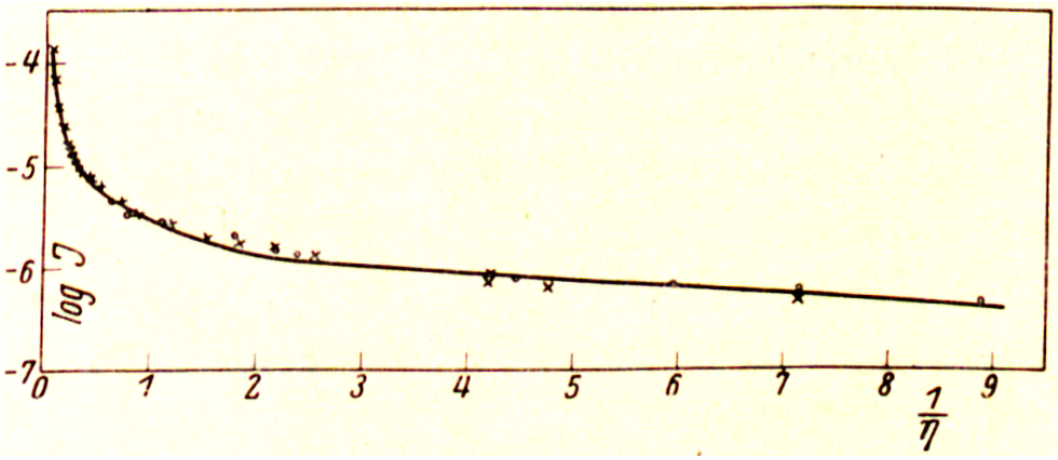


Figure 2: Zn in normal $ZnSO_4$-solution, saturated with H_2 $\left(\log(J) - \frac{1}{\eta}\right)$

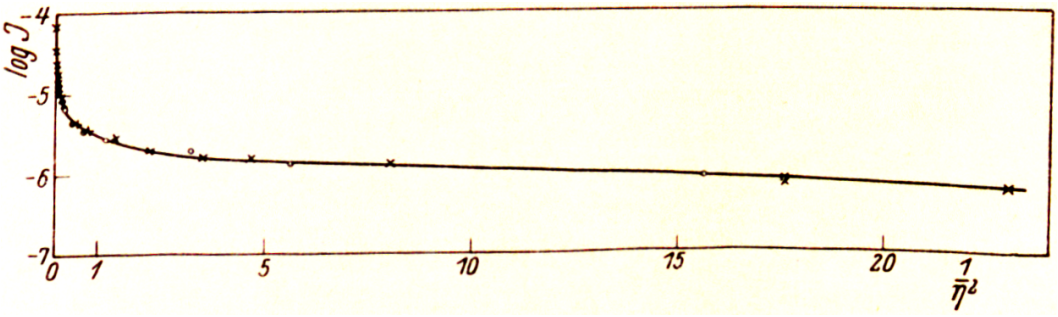


Figure 3: Zn in normal $ZnSO_4$-solution, saturated with H_2 $\left(\log(J) - \frac{1}{\eta^2}\right)$

4 Discussion of Results

Since we first wanted to check whether and which of the characteristics discussed above for small overvoltages corresponded to experience, we examined the current-voltage curves mainly in this area. This investigation has shown that none of the three logarithmic characteristics do justice to the experiments. As a typical example of this, one of the many experiments (we recorded a total of around 200 current-voltage curves under different conditions) is shown here. A zinc sheet electrolytically coated with zinc in the same solution served as the electrode, and normal zinc sulfate solution[2] saturated with hydrogen served as the electrolyte. From the Figure 1, Figure 2 and Figure 3 it can be seen that if $\log(J)$ is plotted against η or against $\frac{1}{\eta}$ or $\frac{1}{\eta^2}$ no straight line is obtained in any case. The fact that the right parts of the $\frac{1}{\eta}$ and $\frac{1}{\eta^2}$ curves are almost straight lines should not be taken as an argument for the correctness of the corresponding equations, since the $\frac{1}{\eta}$ and $\frac{1}{\eta^2}$ scale pulls the curves in these areas very apart. The seemingly straight part only extends from 0.1 mV to 0.3 mV, and of course one cannot draw any conclusions from such a narrow range.

If, on the other hand, we plot the overvoltage against the current density (Figure 4), we see that the initial part of the curve from 0.1 mV to 4 mV results in a straight line. The situation is similar for other metals.

In Figure 4 to Figure 12 two typical current-voltage curves for the metals examined are shown, one with increasing current density ($\times$), the other was recorded immediately following the direction of decreasing current densities ($\bigcirc$).

If we want to interpret the current-voltage curves of electrodeposition, we must take into account an important fact. The current-voltage curves can only provide a relatively simple picture of the electrode process if the size and properties of the electrode surface remain unchanged during the experiment, as is the case, for example, with hydrogen electrolysis. However, this condition is not met in metal electrolysis. As a result of the metal deposition, on the one hand the size of the overall surface changes, and on the other hand the condition of the surface also changes. And this change in surface appears to be one of the most important factors determining the shape of the current-voltage curves.

If we carry out a metal deposition with a small overvoltage (small current density), the supersaturation is small, i.e. the concentration of the ions in the double layer is only slightly larger than corresponds to equilibrium. Under these conditions, metal deposition generally does not occur uniformly over the entire electrode surface, but only at individual active sites. The remaining parts of the electrode surface are not affected by the deposition. As a result, the real current density may be much larger than that apparently calculated from the total surface area. The latter is also not an approximately

[2] Solutions with $c_{eq} = 1\,\mathrm{mol\,L^{-1}}$ were at that times referred to as "normal solutions". c_{eq} is the equivalent concentration.

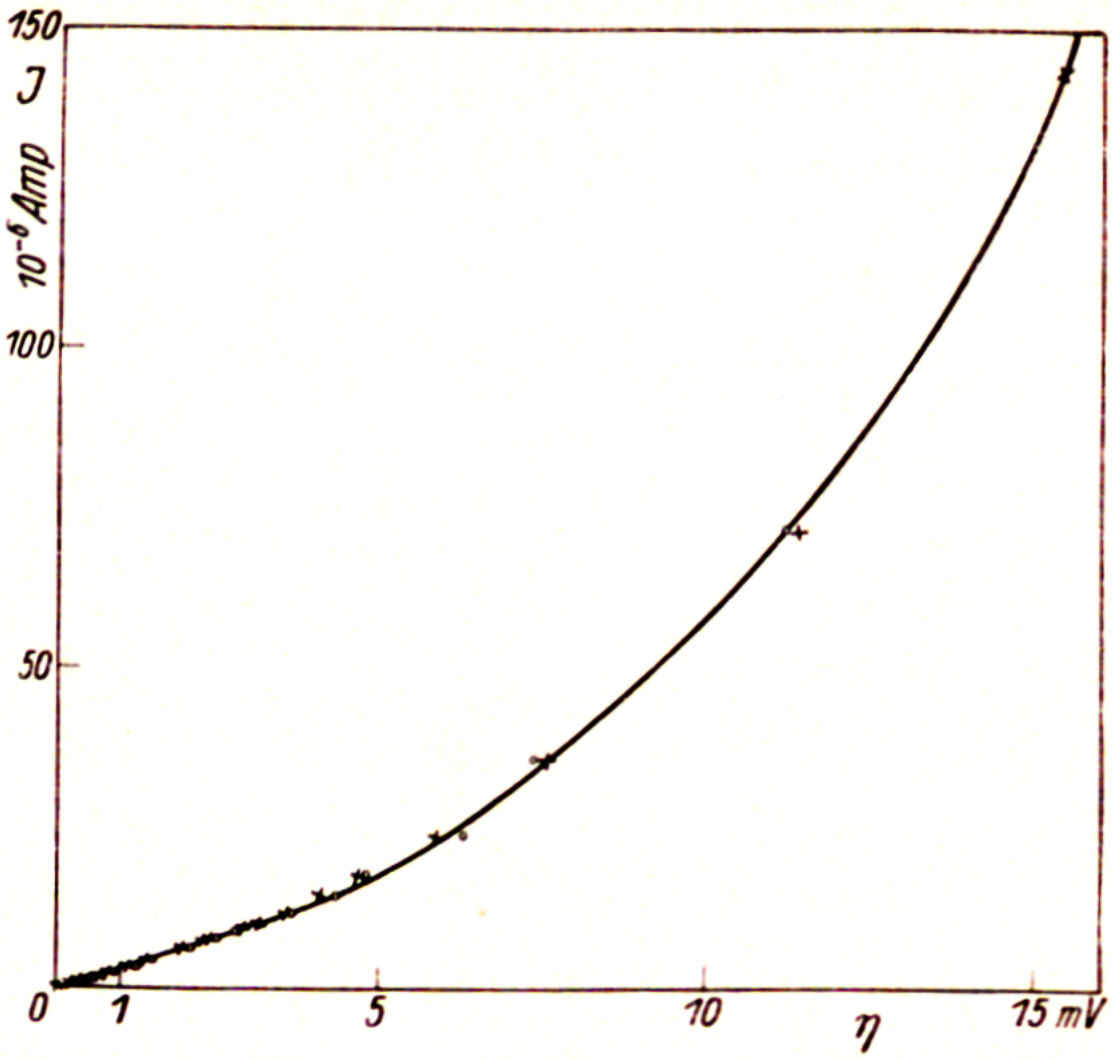


Figure 4: Zn in normal $ZnSO_4$-solution, saturated with H_2 $(J - \eta)$

constant fraction of the former, because the number and extent of the active sites changes with the supersaturation, i.e. with the current density. If one follows the electrolytic metal deposition under the microscope, one can observe directly, what M. Volmer, [9], has already briefly pointed out, with appropriate magnification and lighting, the discontinuous, local growth of the metal crystals. If one looks at a growing crystal surface while an appropriate current strength is applied, one can see that the surface grows in layers. The layer formation begins at one point on the surface, usually at a corner, sometimes at an edge, but never in the middle of the surface. The layers then spread over the surface, and the faster they are, the thinner they are. The growing layers overtaking each other, which creates thicker layers that advance relatively slowly. With appropriately directed lateral illumination, the moving boundaries of the layers can be seen as shadows or as areas of

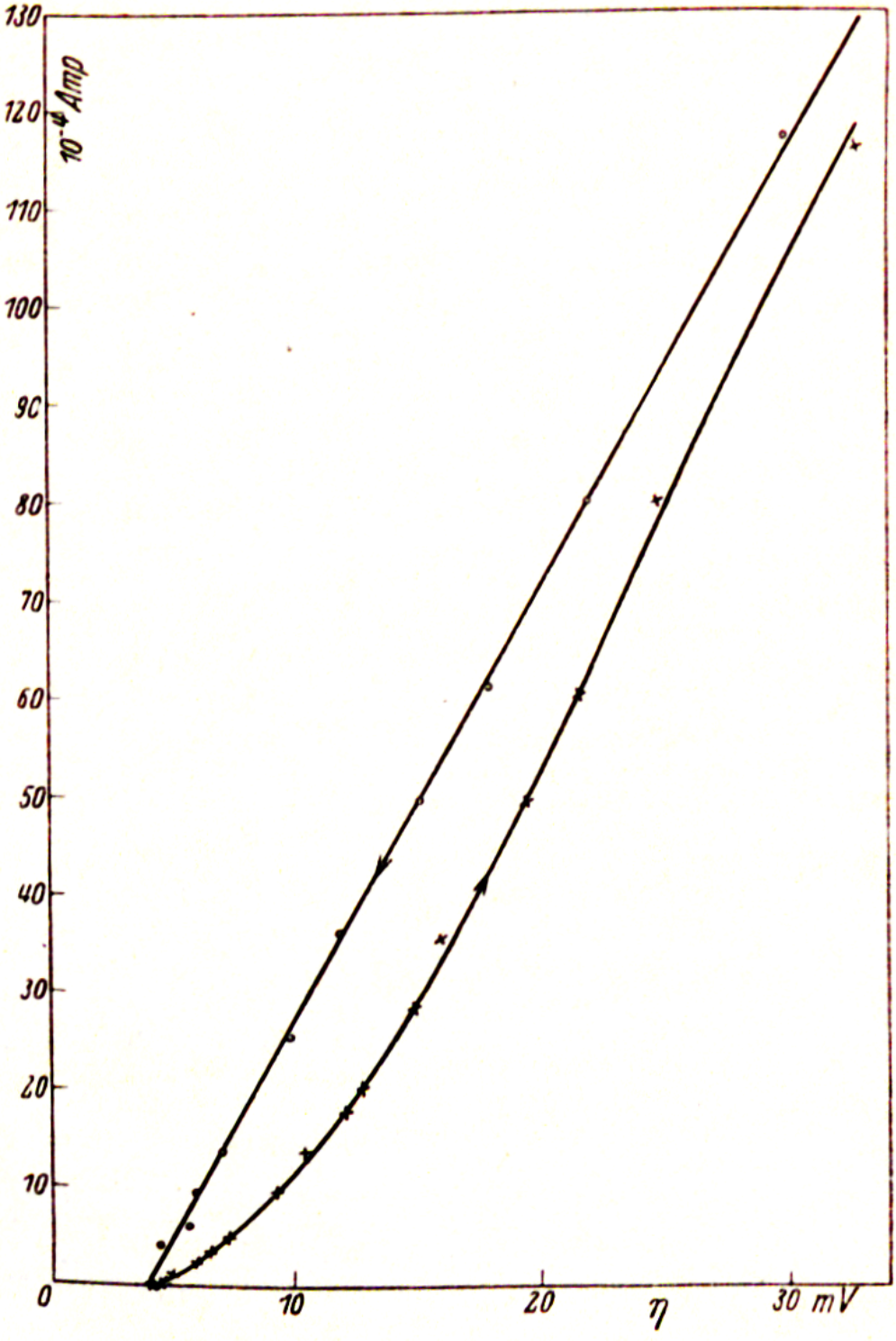
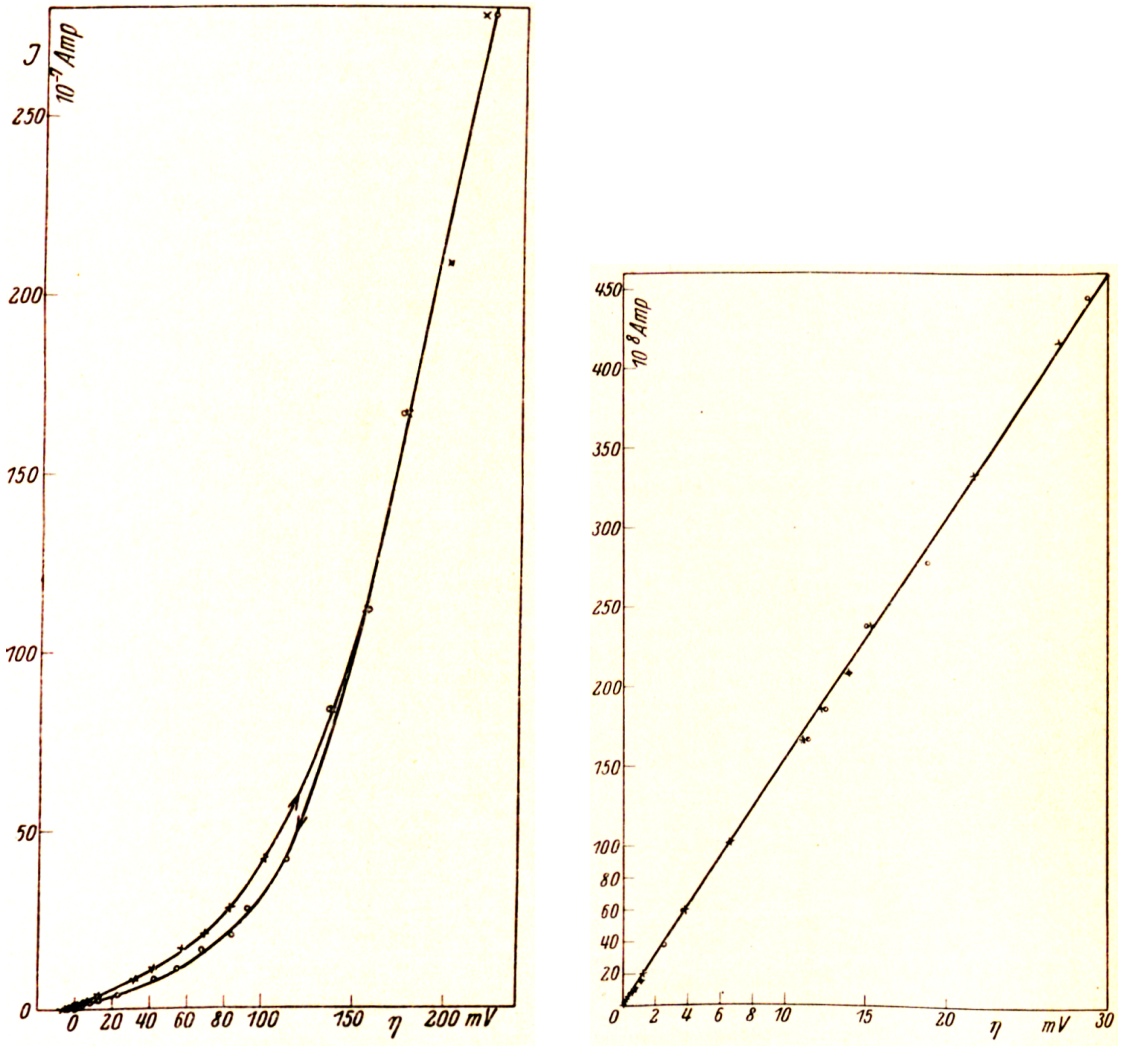


Figure 5: Cd in normal $CdSO_4$-solution, saturated with N_2

increased reflection (depending on the relative position to the light source). Figure 13 shows excerpts from microcinematographic recordings at 250x magnification[3], from the silver deposition from an acidified 2 N silver nitrate solution on a platinum wire at a current of approximately 3×10^{-5} A. One can see on the two surfaces *a* and *b* how new layers begin to form one after the other in the left corner and spread over the surface. On the surface *b* one can also see how the second layer overtakes the first. If one increases the current strength, the steps move faster and their number increases.
The fact that the formation of new layers usually begins at the corners, rarely at the edges, but never in the center of the surface is consistent with STRANSKI's view of the electrolytic growth of metal crystals, [8]. In contrast to growth from vapor, electrolytic growth will not take place from the interior of the surface[4] – as should otherwise be the case with homopolar crystals[5] – but from the corners or edges. There is a significantly greater charge density at the edges and especially at the corners than in the center of the surface. The increased electrostatic attraction at these points increases the attachment energy, so that the first attachment occurs at the corners and edges and the formation of new layers begins at these points. In other words: the high charge density reduces the edge energy so much that the nucleation work becomes very small.

[3]Prof. LEHMANN and Dr. STAMMREICH helped in a courteous manner with the recordings.
[4]The fact that in these experiments nucleation occurs fairly regularly in the middle of the surface is not due to energetic reasons, but is due to the migration of the atoms towards the edge, which makes the supersaturation in the edge region smaller than in the middle.
[5]A crystal characterized by covalent bonding – the type of atomic bonding resulting from the sharing of electrons by neighboring atoms.



(a) Ni in normal acidic $NiSO_4$-solution, saturated with H_2

(b) Ni in normal acidic $NiSO_4$-solution, saturated with H_2. The first rectilinear part on a larger scale

Figure 6:

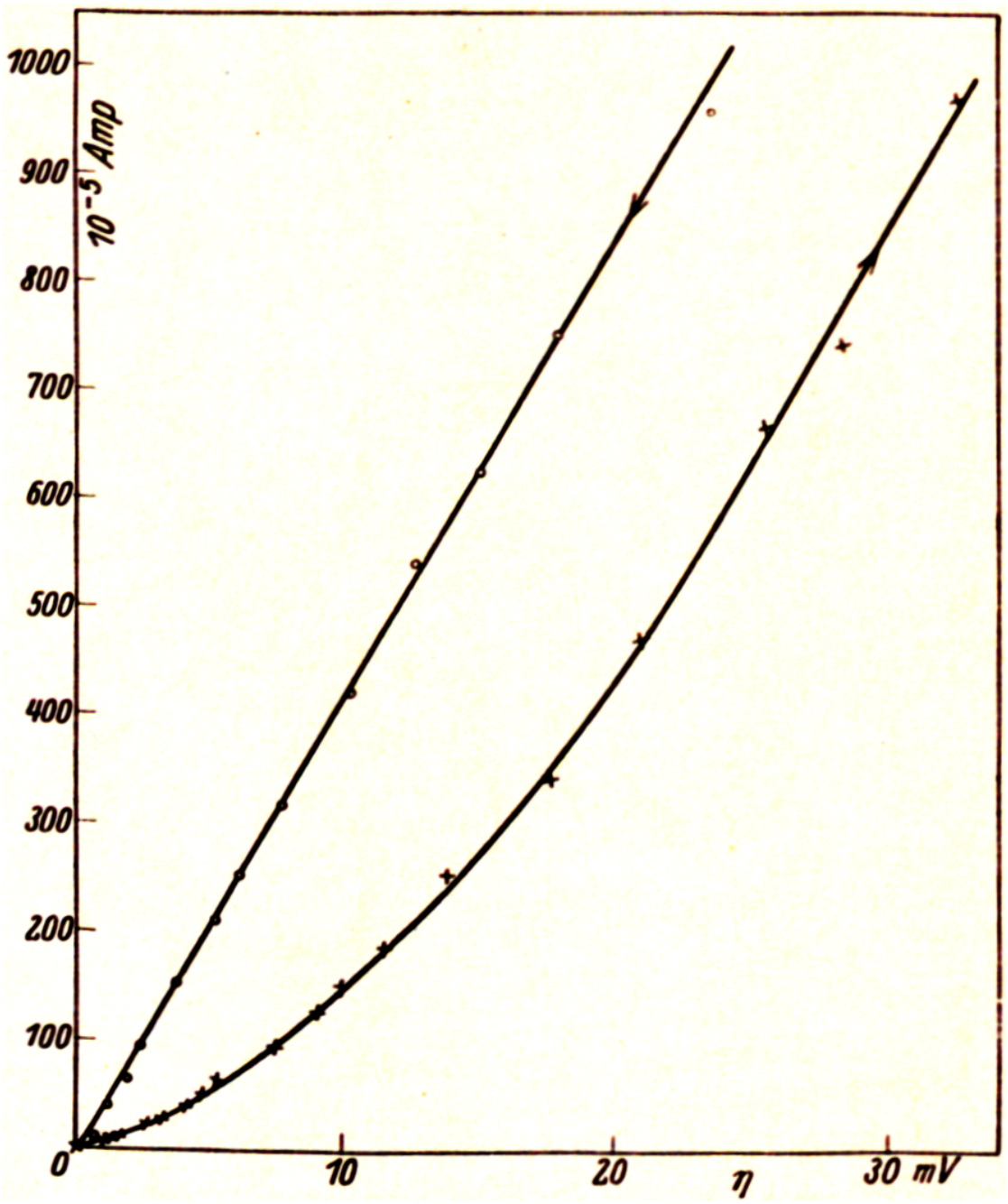


Figure 7: Pb in normal acetic acid lead acetate-solution, saturated with N_2

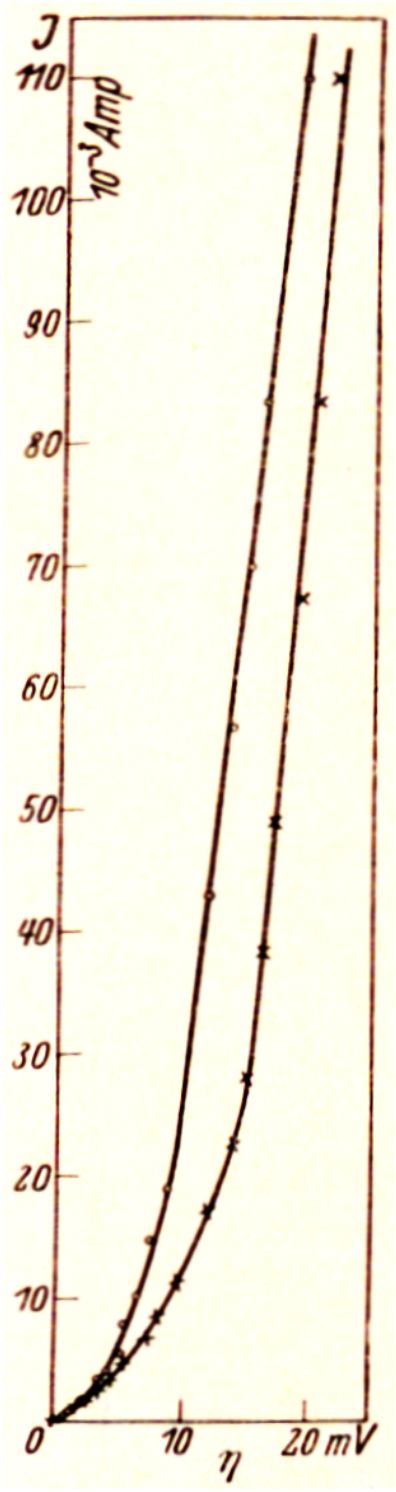


Figure 8: Bi in normal acidic $BiCl_3$-solution, saturated with N_2

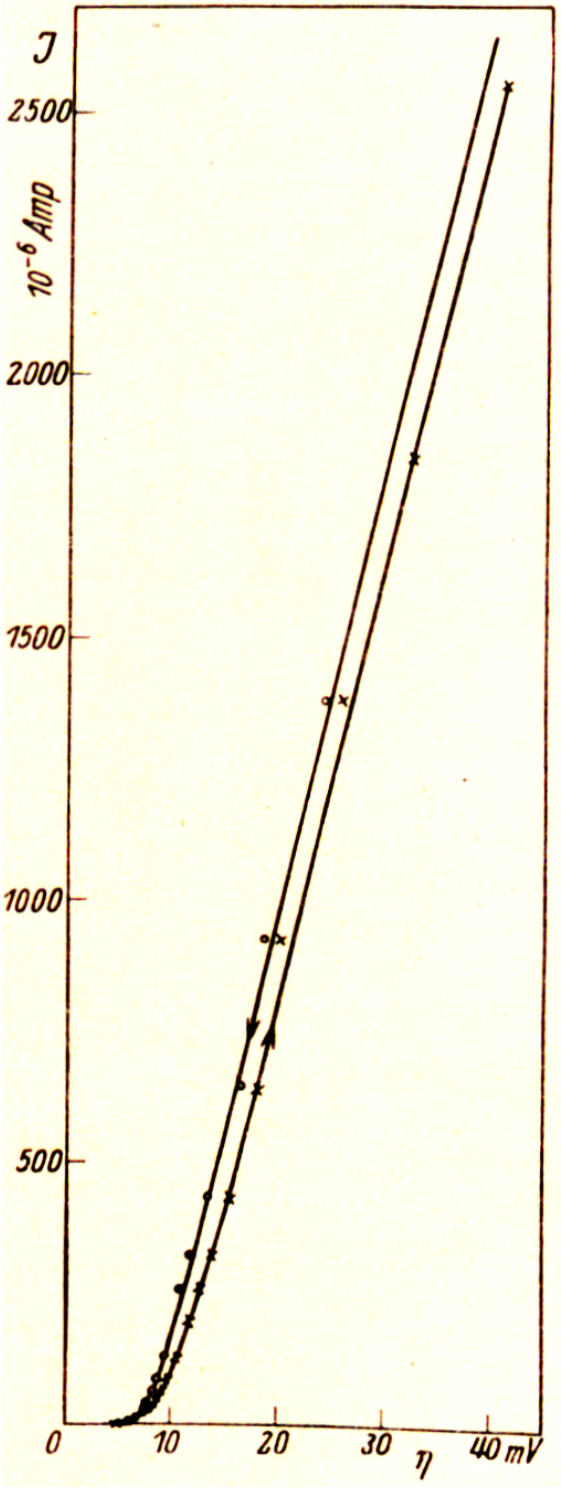


Figure 9: Cu in normal acidic $CuSO_4$-solution, saturated with N_2

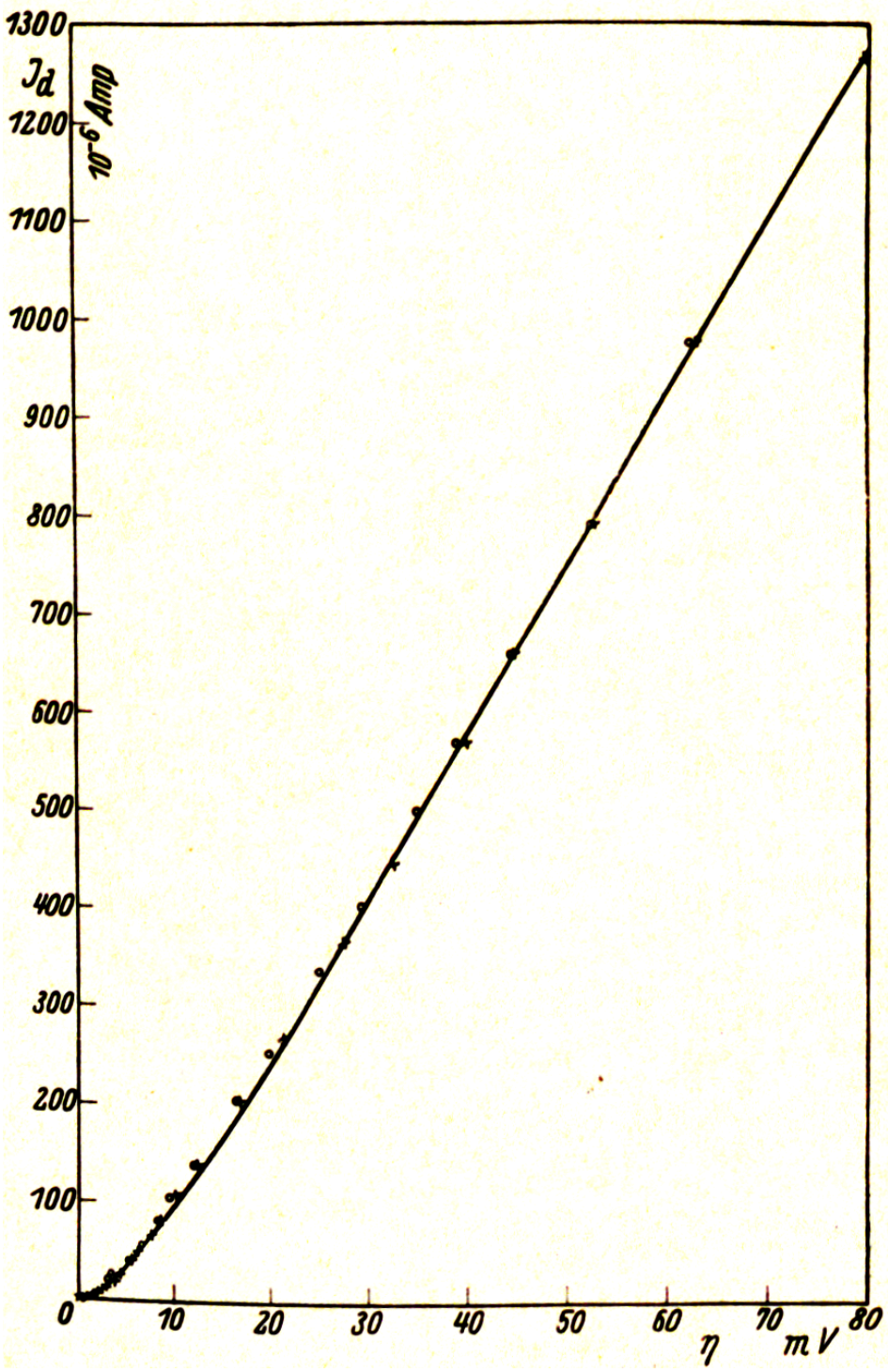


Figure 10: Ag in normal acidic $AgNO_3$-solution, saturated with N_2

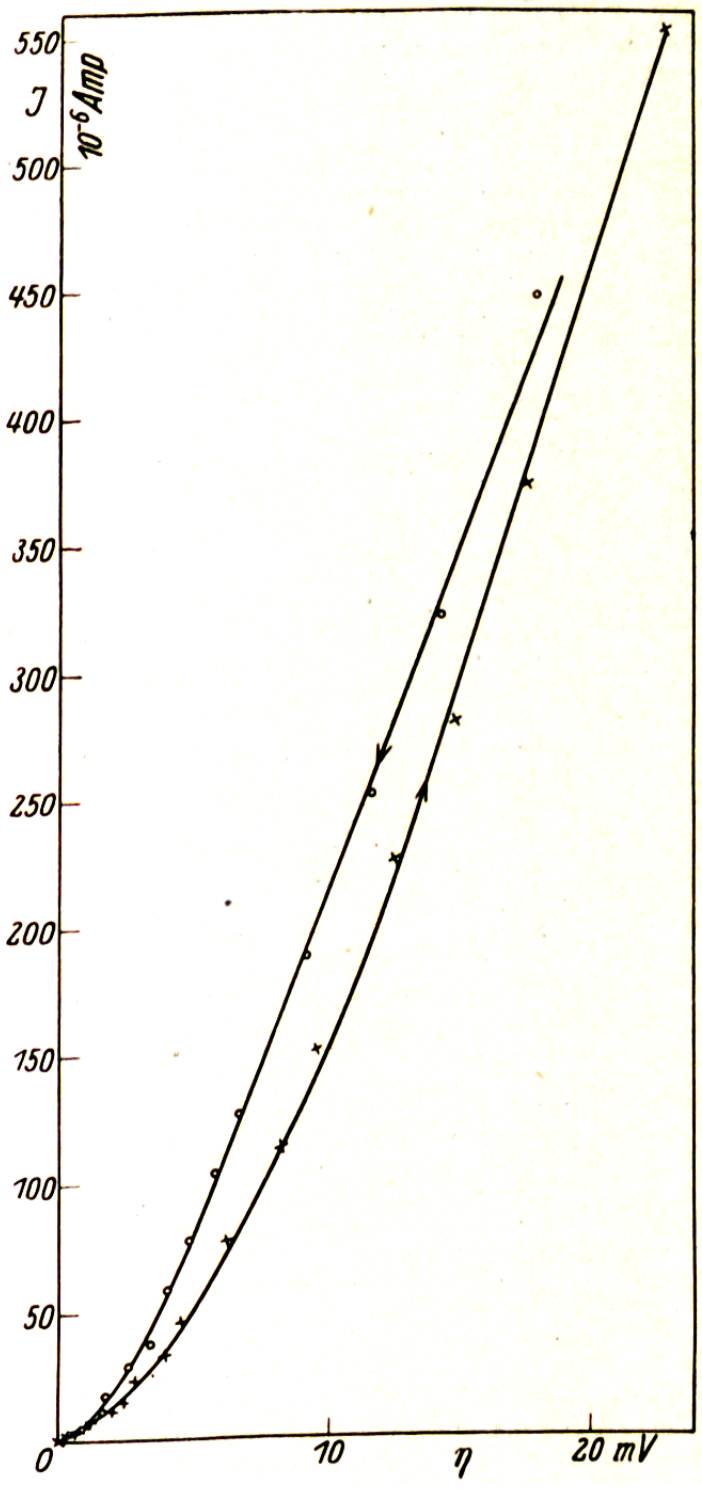


Figure 11: Ag in $KAgCy_2$-solution, saturated with N_2

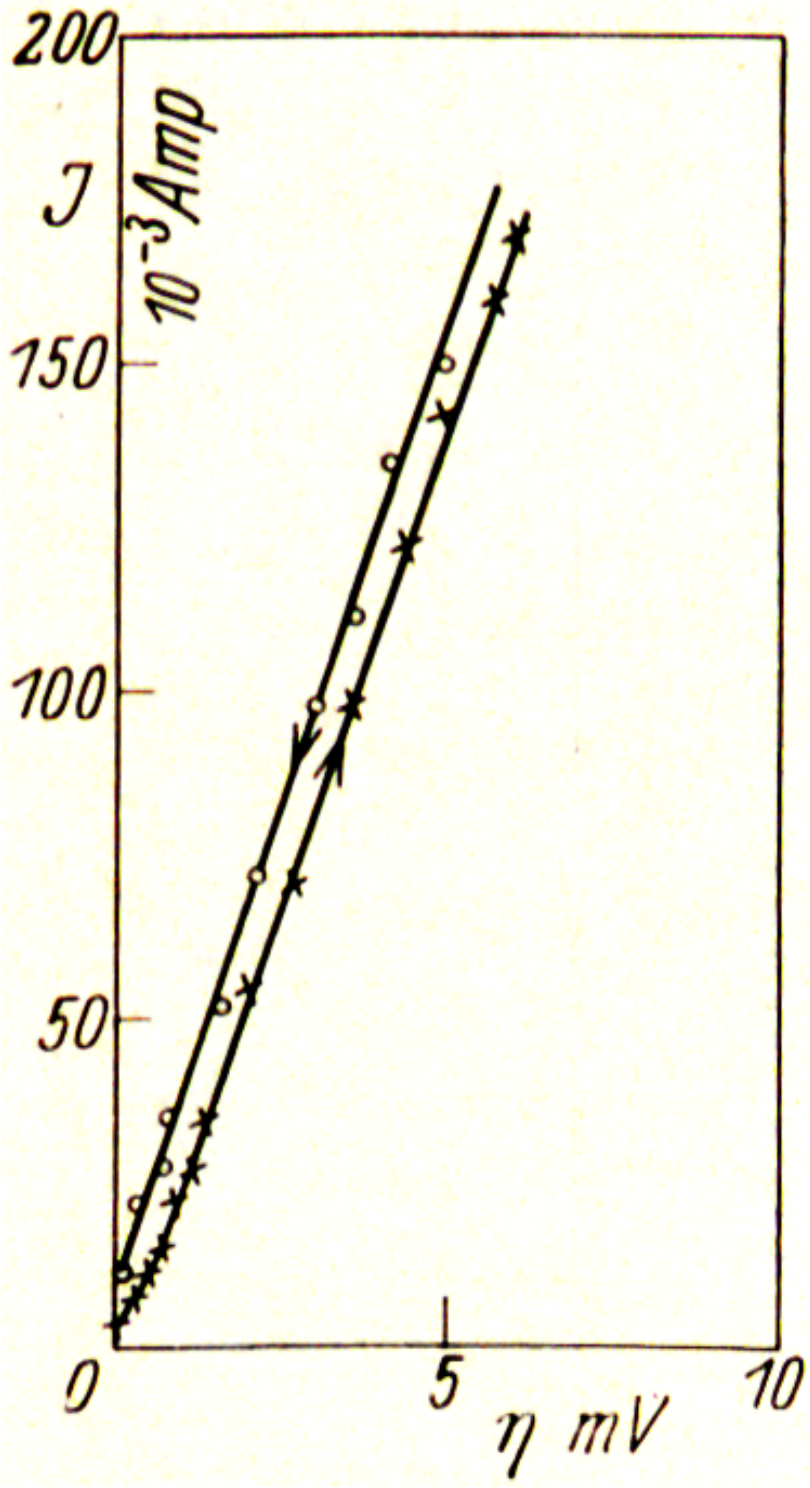


Figure 12: Ag in melted $AgNO_3$, (220 °C)

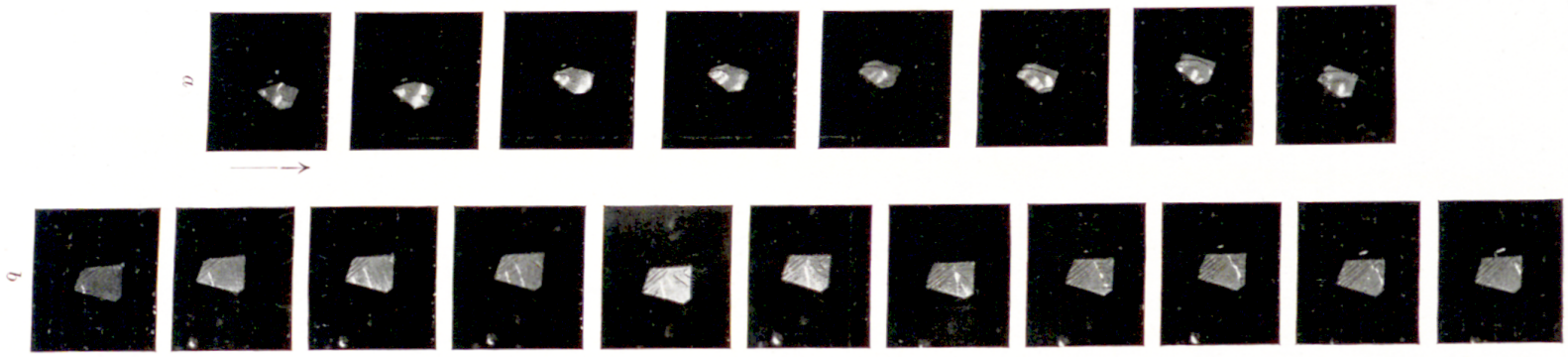


Figure 13: Microcinematographic recordings of electrolytically growing silver crystals (250x magnification)

However, as the experiment shows, there is now no continuous new creation of layers, but rather the process appears to be periodic. If the new attachment has led to the formation of a layer of microscopically visible thickness, the new creation apparently stops and the deposition predominates at the created step that advances over the surface at a certain speed at a noticeably constant height. One could see the explanation for this in the local ion depletion associated with deposition, and through which the site of easiest deposition moves from the crystal corner with depleted surrounding to the step with unused solution.
We tried to observe these optically detected discontinuities electrically, namely through sensitive oscillographic recordings of voltage- or current strength-time curves, but without success[6]. This shows that the initiation of new layers at the corners is not opposed by any noticeable two-dimensional nucleation inhibitions, in agreement with the failure of the law tested under such assumptions (see page 3). On the other hand, nucleation on the interior of the surface is so difficult that it is not noticeable at all. This difficulty causes the smoothness of the crystal surface.
The entire electrolysis takes place through deposition at the active sites. These make up a small fraction of the total surface area, which increases as the current density increases. The claim that a small part of the surface is active is based on the microscopic observations and on the agreement with the current-voltage curve. After an approximately rectilinear increase, these show a further course that is just in the opposite direction to that expected with concentration polarization. A rectilinear current-voltage curve would be expected for a point-shaped electrode in an electrolyte solution that is not too diluted or in a melt. The ideal case would be a linear chain of atoms that only allows extension at one end. In this case diffusion is a rapid process, so that the nature of the electrolyte in the surrounding of the ever-advancing active site remains constant. Then the speed of the ion supply is proportional to the acting force, i.e. one gets a linear relationship between current and voltage like Ohm's law. Metal deposition comes close to this ideal case (especially for metals with high overvoltage) at the smallest current densities, at which the electrode could be idealized by a number of such chains of atoms, corresponding to the majority of the active points. As the overvoltage increases, periodic step formation occurs more frequently

[6]Mr Kromrey made careful attempts to use an extensive amplifier system to detect acoustically any possible voltage fluctuations during electrolytic crystal growth. In fact, a quiet, characteristic noise was noticeable, which disappeared when switching to a mercury cathode of the same size. The insignificance of the effect made further pursuit seem pointless. In particular, it proved impossible to establish a relationship between acoustic frequency and the number of lattice planes formed per second, which was originally intended.

and the surface becomes increasingly rough. Hence, the number of active sites increases with the overvoltage, which results in the observed quasi-autocatalytic increase in current strength. This autocatalytic increase must become weaker again as soon as the roughness has reached such a high level that only a small increase in the number of active sites can take place. Then the increase must become noticeably rectilinear again until concentration polarization finally sets in.
The deviation from rectilinearity actually disappears if it is ensured that the surface of the electrode cannot change with the current strength. This can be seen in the behavior of mercury electrodes, which, according to the experiments of HEYROVSKY and co-workers, [5], which we can confirm, provide a straight-line current-voltage curve. It can also bee seen in the experiments of HOEKSTRA, [4], namely when the electrode is constantly scraped. In both cases, after the initial straightness of the characteristics, a bending in the sense of concentration polarization is obtained, i.e. an opposite curvature to that of the crystalline metals discussed above.

5 Summary

In connection with the consideration of the various possibilities of the partial process of deposition of ions that determines the rate of electrolytic metal deposition, the characteristics for the following cases were discussed:

1. The *discharge of ions* is the rate-determining process: Characteristic: $\log(J) \sim \eta$.
2. The *frequency of two-dimensional nucleation* is the slowest process: $\log(J) \sim \frac{1}{\eta}$.
3. The *frequency of three-dimensional nucleation* is the slowest process: $\log(J) \sim \frac{1}{\eta^2}$.
4. The *layered growth* of the nuclei is crucial for the rate of deposition: $J \sim \eta$.

The experiment decided on point 4. It was shown on the basis of the current-voltage curves of Zn, Cd, Ni, Pb, Bi, Cu and Ag examined at small overvoltages as well as through the microcinematographic recordings of the electrolytic growth of crystals that when the change in the active sites and the overall surface is taken into account the current-voltage curves can be explained under the assumption that the overvoltage is linearly associated with the real current density.

The implementation of the work was gratefully supported by funds from the Notgemeinschaft.

Berlin, Institute for physical chemistry and electrochemistry at the Technical College.

References

[1] H. Brandes. Zur Theorie des Kristallwachstums. *Zeitschrift für physikalische Chemie*, 126(3-4):196–210, 1927.

[2] H. Brandes. Elektrolytische Polarisationen aus Anlass von Kristallwachstumshemmungen. *Zeitschrift für physikalische Chemie (A)*, 142(2):97–112, 1929.

[3] T. Erdey-Grúz and M. Volmer. Zur Theorie der Wasserstoff Überspannung. *Zeitschrift für physikalische Chemie (A)*, 150(1):203–213, 1930.

[4] J. Hoekstra. The electrolysis of metals, studied with a scraped electrode. *Collection of Czechoslovak Chemical Communications*, 6:17–36, 1934.

[5] W. Kemula. Polarographic studies with the dropping mercury kathode. Part XI. Overpotential of mercury deposited from mercuric salt solutions. *Collection of Czechoslovak Chemical Communications*, 2:347–362, 1930.

[6] M. Le Blanc. *Die elektromotorischen Kräfte der Polarisation und ihre Messung mit Hilfe des Oszillographen*, volume 3 of *Abhandlungen der Deutschen Bunsen-Gesellschaft für angewandte physikalische Chemie*, page 79. Wilhelm Knapp Verlag, Halle an der Saale, 1910.

[7] M. Le Blanc and K. Schick. Über Elektrolyse mit Wechselströmen. *Zeitschrift für Elektrochemie*, 9(32):636–641, 1903.

[8] Stranski. Beitrag zum Wachstum und Auflösen nichtpolarer Kristalle. *Zeitschrift für physikalische Chemie (B)*, 11(4):342–349, 1931.

[9] M. Volmer. Zum Problem des Kristallwachstums. *Zeitschrift für physikalische Chemie*, 102(3-4):267–275, 1922.

[10] M. Volmer and A. Weber. Keimbildung in übersättigten Gebilden. *Zeitschrift für physikalische Chemie*, 119(3-4):277–301, 1926.